

**DESCRIPTION**

Resin composition and multi-layer article thereof

**5 Technical Field**

The present invention relates to a resin composition that is superior in antistatic properties, processability and compatibility, and a multi-layer article thereof.

**10 Background Art**

In general, molded articles produced from polymer materials readily generate static electricity and often collect dust from air while they are handled in storage, transit, and end uses, which result in pollution of the surface of molded articles. In the case that the molded article is a bag for powders and the like, a part of the contained powders sticks to the internal surface of the bag, often defacing the package and impairing the commercial value of the merchandise. To prevent the adhesion of dust and powders, various kinds of antistatic technologies have been proposed and put into practice.

Generally adopted approaches include a method to melt-blend an antistatic agent into the molding resin composition and a method to coat the molded articles with an antistatic agent or an antistatic polymer. Those methods, however, are known to have some drawbacks. For instance, the former method is often accompanied by contamination of the packaged material with bleed out of the migrated antistatic agents or the problem of

time-related deterioration in the antistatic properties. As for the latter method, some defects are pointed out such as poor water resistance of the coated layer, easy damage of the coated layer, increase in surface tackiness resultant from water absorption, etc.

5 To improve such a drawback, a method to blend potassium ionomer which is a macromolecular antistatic agent is known. For example, Japanese Laid-open Patent Application No. 3-106954 proposed potassium ionomer of two or more kinds of 10 ethylene-unsaturated carboxylic acid copolymers having different unsaturated carboxylic acid contents. And it is clarified that superior antistatic properties are shown when the ionomer is compounded into other thermoplastic resin, specifically such as ethylene-vinyl acetate copolymer and low 15 density polyethylene.

In addition, Japanese Laid-open Patent Application No. 4-93340 proposed an olefin polymer composition having superior antistatic properties, wherein potassium ionomer contained a high potassium ion content is blended with an olefin polymer 20 or a copolymer of olefin and unsaturated ester. Concretely the example that potassium ionomer aforementioned is blended with ethylene-vinyl acetate copolymer or low density polyethylene is shown.

By the way, when potassium ionomer as above-mentioned is 25 blended in polyolefin type resin having high crystallinity, widely used in the field of film and blow molded container, such as polyethylene, especially high density polyethylene, and

polypropylene, the following drawbacks are often observed. Namely melt torque of an extruder increases and productivity falls in molding processing due to poor dispersibility and compatibility of potassium ionomer, and it is easy to cause  
5 bad-appearance of molded articles.

Therefore the object of the present invention is to provide a method to improve processability without impairing physical properties of high crystalline polyolefin type resin and obtain molded articles having a good-appearance when potassium ionomer  
10 is blended.

#### **Disclosure of the Invention**

The present invention relates to a resin composition comprising 5 to 50 parts by weight of a potassium ionomer (A) of an ethylene-unsaturated carboxylic acid copolymer (ethylene-unsaturated carboxylic acid copolymer, neutralized with potassium ion and sometimes called simply as potassium ionomer hereinafter), 0.5 to 20 parts by weight of an ethylene-unsaturated ester copolymer (B) and 94.5 to 30 parts  
15 by weight of a thermoplastic resin (C) other than (A) and (B).  
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#### **Preferred Embodiments of the Invention**

The ethylene-unsaturated carboxylic acid copolymer used as a base polymer of the potassium ionomer (A) of the present  
25 invention is produced by copolymerizing ethylene with an unsaturated carboxylic acid and further optionally with another polar monomer.

As unsaturated carboxylic acid, acrylic acid, methacrylic acid, fumaric acid, maleic anhydride, monomethyl maleate, monoethyl maleate, etc. can be exemplified here. Acrylic acid or methacrylic acid is particularly preferable. In addition,

5 as another polar monomer which can optionally be copolymerized, a vinyl ester such as vinyl acetate, vinyl propionate; an unsaturated carboxylic acid ester such as methyl acrylate, ethyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, isoctyl acrylate, methyl

10 methacrylate, ethyl methacrylate, dimethyl maleate, diethyl maleate; carbon monoxide, etc. can be cited. In particular, an unsaturated carboxylic acid ester, especially (meth)acrylic acid ester is a suitable copolymerization component.

The above ethylene-unsaturated carboxylic acid copolymer

15 can be obtained by radical copolymerization of ethylene and unsaturated carboxylic acid with other optional polar monomers under high temperature and high pressure.

In cases where the ethylene-unsaturated carboxylic acid copolymer used as the base polymer of the potassium ionomer has

20 an excessively small acid content or the potassium ionomer has an excessively low degree of neutralization, it is not easy to obtain a resin composition having superior antistatic properties. It is, therefore, preferable to use one type or two or more types of potassium ionomers of ethylene-unsaturated carboxylic acid

25 copolymer, where the unsaturated carboxylic acid content of the base ethylene-unsaturated carboxylic acid copolymer (or the average unsaturated carboxylic acid content of the base

ethylene-unsaturated carboxylic acid copolymers) is 10 to 30% by weight, and preferably 10 to 20% by weight, and the degree of neutralization with potassium ion is 60% or more (60 to 100%), and preferably 70% or more (70 to 100%). Especially it is desirable  
5 to use the mixture of two or more types of potassium ionomers of ethylene-unsaturated carboxylic acid copolymers having different average acid contents.

An example is mixed ionomers, having 60% or more, preferably 70% or more, of neutralization degree by potassium ion, of two or more types of ethylene-unsaturated carboxylic acid copolymers having difference in acid contents between the highest content and the lowest content of 1% by weight or more, preferably 2 to 20% by weight, and having an average acid content of 10 to 30% by weight, preferably 10 to 20% by weight. More  
10 specifically, particularly preferred example is mixed ionomers having the aforesaid neutralization degree (60% or more), of the mixed copolymer components that have an average unsaturated carboxylic acid content of 10 to 30% by weight, preferably 10 to 20% by weight, and an average melt flow rate of 1 to 300 g/10  
15 min, more preferably 10 to 200 g/10 min, further preferably 20 to 150 g/10 min, as determined in accordance with JIS K 7210-1999 at a temperature of 190°C and under a load of 2,160 g, wherein the mixed copolymer components comprise an ethylene-unsaturated carboxylic acid copolymer (A-1) having an unsaturated carboxylic  
20 acid content of 1 to 10% by weight, preferably 2 to 10% by weight, and a melt flow rate of 1 to 600 g/10 min, preferably 10 to 500 g/10 min, as determined at a temperature of 190°C and under a

load of 2,160 g and an ethylene-unsaturated carboxylic acid copolymer (A-2) having an unsaturated carboxylic acid content of 11 to 25% by weight, preferably 13 to 23% by weight, and a melt flow rate of 1 to 600 g/10min., preferably 10 to 500 g/10 min, as determined at a temperature of 190°C and under a load of 2,160 g. It is preferable that the copolymer compositions is prepared by blending A-1 and A-2 in the ratio of 2 to 60 parts by weight, preferably 5 to 50 parts by weight, for A-1, and 98 to 40 parts by weight, preferably 95 to 50 parts by weight, for 10 A-2. In addition, the average melt flow rate mentioned above is a melt flow rate of the melt-blended mixture of A-1 and A-2.

The ethylene-unsaturated carboxylic acid copolymer, as a base polymer of the potassium ionomer, may contain another polar monomer as has already been mentioned. For instance, a 15 multi-component copolymer containing another polar monomer in the range of 40% by weight or less, preferably 30% by weight or less can be used.

It is also preferable to use a potassium ionomer having a melt flow rate of 0.1 to 100 g/10 min, and particularly 0.2 to 50 g/10 min as determined in accordance with JIS K 7210-1999 20 at a temperature of 190°C and under a load of 2,160g in consideration of its processability and miscibility with other components.

As the component (B) of the resin composition in the present 25 invention, an ethylene-unsaturated ester copolymer is used. As unsaturated ester of the ethylene-unsaturated ester copolymer, vinyl ester such as vinyl acetate and vinyl propionate;

unsaturated carboxylic acid ester such as methyl acrylate, ethyl acrylate, isopropyl acrylate, isobutyl acrylate, n-butyl acrylate, isoctyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate and isobutyl methacrylate can be cited. Above all, suitable unsaturated ester is unsaturated carboxylic acid ester, and especially acrylic acid ester or methacrylic acid ester.

In the copolymer (B), an unsaturated ester content is preferably 5 to 40% by weight, particularly 10 to 35% by weight, and a melt flowrate is preferably 0.1 to 100 g/10 min, particularly 0.2 to 50 g/10 min as determined in accordance with JIS K 7210-1999 at a temperature of 190°C and under a load of 2,160g to impart sufficient improvements in processability and compatibility.

The thermoplastic resin (C) used in the present invention is a thermoplastic resin except potassium ionomer (A) and ethylene-unsaturated ester copolymer (B). Namely, olefin polymer including polyolefin type resins such as homopolymer of ethylene or copolymer of ethylene with  $\alpha$ -olefin having 3 to 12 carbon atoms, for example, high pressure polyethylene, medium/high density polyethylene, linear low density polyethylene, very low density polyethylene; polypropylene, poly-1-butene, poly-4-methyl-1-pentene and polyolefin type elastomer; styrene type polymers such as polystyrene, rubber reinforced styrene resin such as high-impact polystyrene and ABS resin; polyesters such as polyethylene terephthalate, polytrimethylene terephthalate, polytetramethylene terephthalate, polyethylene naphthalate, polyethylene

terephthalate copolymerized with cyclohexane dimethanol, polyester elastomer; polycarbonate, polymethyl methacrylate or two or more kinds of mixtures of these can be exemplified.

In the above other thermoplastic resin (C), polyolefin type resins, particularly medium/high density polyethylene, high crystalline polypropylene, high crystalline poly-4-methyl-1-pentene are desirable. Above all, it is more desirable to choose medium/high density polyethylene.

The medium/high density polyethylene is homopolymer or copolymer of ethylene with  $\alpha$ -olefin having 3 or more carbon atoms, has a density of 935 kg/m<sup>3</sup> or more, preferably 940 to 970 kg/m<sup>3</sup>, and can be produced by medium or low pressure method. In addition, in consideration of processability and practical physical properties, it is preferable to use one having a melt flow rate of 0.1 to 100 g/10 min, and particularly 0.2 to 50 g/10 min, as determined in accordance with JIS K 7210-1999 at a temperature of 190°C and under a load of 2,160 g.

As the  $\alpha$ -olefin having 3 or more carbon atoms in the above ethylene copolymer, propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecen and 4-methyl-1-pentene can be cited. Particularly copolymer of  $\alpha$ -olefin having around 3 to 12 carbon atoms is preferably used.

As the crystalline polypropylene which can be used for (C) component, homopolymer of propylene and copolymer of propylene as major component and other  $\alpha$ -olefin can specifically be cited. And the copolymer may be a random copolymer or a block copolymer. As other  $\alpha$ -olefin in the copolymer of propylene,

$\alpha$ -olefin having 2 to 20 carbon atoms such as ethylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene and 4-methyl-1-pentene can be cited. Such other  $\alpha$ -olefin can be copolymerized singly or in the combination of two or more kinds. In addition, in consideration of processability and practical physical properties, it is preferable to use polypropylene having a melt flow rate of 0.1 to 100 g/10 min, and particularly 0.2 to 50 g/10 min as determined in accordance with ASTM D 1238 at a temperature of 230°C and under a load of 2,160 g.

As the above crystalline polypropylene, it is particularly preferable to use homopolymer or a random copolymer of propylene and ethylene. In the random copolymer of propylene and ethylene, the copolymer having ethylene content of, for example, 0.1 to 10 mol%, particularly 0.5 to 5 mol% is preferable. Moreover, in the random copolymer of propylene and ethylene, it may be a multi-component random copolymer in which  $\alpha$ -olefin having 4 or more carbon atoms such as 1-butene is further copolymerized.

The crystalline polypropylene can be obtained by polymerization of propylene or copolymerization of propylene and (an)other  $\alpha$ -olefin in the presence of a stereospecific catalyst. For instance, the crystalline polypropylene can be produced using a polymerization catalyst such as a Ziegler-Natta catalyst comprising a highly active titanium catalyst component containing electron donor, an organoaluminum compound and an electron donor, and a single-site catalyst comprising a metallocene compound containing electron donor and an aluminoxane.

The resin composition of the present invention comprises a potassium ionomer (A) of 5 to 50 parts by weight, preferably 10 to 40 part by weight, an ethylene-unsaturated ester copolymer (B) of 0.5 to 20 parts by weight, preferably 1 to 10 part by 5 weight and a thermoplastic resin (C) of 30 to 94.5 parts by weight, preferably 1 40 to 85 part by weight, based on 100 parts by weight in total of the potassium ionomer(A), the ethylene/unsaturated ester copolymer(B) and the thermoplastic resin (C) other than (A) and (B). When the blend ratio of the potassium ionomer is 10 too small, the composition having superior antistatic properties may become hard to be obtained. In addition, combining the ethylene-unsaturated ester copolymer (B) in the above blend ratio is effective to improve compatibility of (A) and (C). However, when ethylene-unsaturated ester copolymer (B) is combined too 15 much, further increase in the effect is not expected and it may impair superior properties of (C).

Various additives can be compounded in the resin composition of the present invention as required. As an example of such additives, antioxidants, light stabilizers, ultraviolet 20 absorbers, pigments, dye stuffs, lubricants, anti-blocking agents, inorganic fillers, foaming agents, foaming promoters, crosslinking agents can be exemplified.

The resin composition of the present invention can be used as various kinds of molded articles. In that case, the resin 25 composition can be used as a single (mono) layer article, or as a multi-layer article with another material. In such a multi-layer article, the resin composition can be used as a

surface layer or a middle layer. In a bag or blow molded article, the resin composition can be used not only as an outer surface layer and an inner surface layer, but also as a middle layer. As the layer of the other material that can be used for the above

5 multi-layer article, a layer of a thermoplastic resin (D) other than the resin composition of the present invention can be used.

The thermoplastic resin (D) can comprise the ethylene-unsaturated ester copolymer (B) in the resin composition of the present invention or the thermoplastic resin

10 (C).

The layer of the other material may be a recycled resin layer formed from reject products or scrap materials such as trimmed edges produced in manufacturing the multi-layer article, or an adhesive layer. Since the material for such a recycled

15 resin layer is basically equal with materials constituting the multi-layer article or a mixture thereof, and have good compatibility with at least one material of the multi-layer article, it can be expected that the material contribute to improve the adhesiveness between layers. As a material for the

20 above adhesive layer usable as a layer constituting the multi-layer article, any materials which improve interlaminar adhesiveness can be used. As such a material, a hot-melt type adhesive or a coating type adhesive may be cited. It is industrially preferable to use an extrusion type adhesive  
25 selected from a thermoplastic resin, a composition thereof with a tackifier, etc.

As the thermoplastic resin (D) as the other material that

constitutes the multi-layer article, an olefin polymer selected from a homopolymer of olefin, a copolymer of two or more kinds of olefins and a copolymer of olefin and a polar monomer is preferable. Especially a polyolefin type resin such as

5 polyethylene and polypropylene is most preferable. The thickness ratio of layers of the multi-layer article can be chosen appropriately. For example, the thickness ratio of layer of the resin composition of this invention / layer of other materials can be about 0.1 to 1000, preferably about 0.5 to 100. In addition,

10 total thickness can vary depending on the purpose of use, and for example, preferred thickness is about 10 to 5000  $\mu\text{m}$ , preferably about 100 to 3000  $\mu\text{m}$ . The aforementioned multi-layer article can be produced, preferably by laminating each layer using a technique such as extrusion coating, film or sheet

15 coextrusion and coextrusion blow molding. In case the resin composition of the present invention is used as a single layer article, preferred thickness of the article is about 10 to 5000  $\mu\text{m}$ , preferably about 100 to 3000  $\mu\text{m}$ .

20 [Examples]

The present invention is explained in more detail with examples below.

Raw materials and test methods for evaluating physical properties used in the examples and comparative example are as

25 mentioned hereafter.

1. Raw materials

- (1) IO: Ionomer which is a potassium ionomer, having a neutralization degree of 85% and MFR (measured by JIS K 7210-1999 at 190°C under a load of 2160 kg, same hereunder) of 0.3 g/10 min, of a blend, having an average methacrylic acid content of 16.5% by weight and average MFR of 265 g/10 min, composed of 45 parts by weight of ethylene-methacrylic acid copolymer having methacrylic acid content of 20% by weight and MFR of 500 g/10 min, 27 parts by weight of ethylene-methacrylic acid copolymer having methacrylic acid content of 15% by weight and MFR of 60 g/10 min and 18 parts by weight of ethylene-methacrylic acid copolymer having methacrylic acid content of 10% by weight and MFR of 100 g/10 min
- (2) EEA: Ethylene-ethyl acrylate copolymer (ethyl acrylate content: 19% by weight, MFR: 5 g/10 min)
- (3) EMA: Ethylene-methyl acrylate copolymer (methyl acrylate content: 16% by weight, MFR: 9 g/10 min)
- (4) HDPE: High density polyethylene (Trade name: Hizex 6200B, manufactured by Mitsui Chemicals, Inc., density: 956 kg/m<sup>3</sup>, MFR: 0.36 g/10 min)
- (5) Resin composition
- (A) Composition 1: IO/EEA/HDPE=18/2/80 (weight ratio)
  - (B) Composition 2: IO/EEA/HDPE=9/1/90 (weight ratio)
  - (C) Composition 3: IO/EMA/HDPE=13.5/1.5/85 (weight ratio)

2. Test items and methods for evaluation

Three-layer containers, having inner volume of 100ml and having layer construction, total thickness and thickness ratio

shown in Table 1, were formed using a three-layer blow-molding machine. And evaluation on items described below was conducted.

(1) Electric potential measurement

(a) The surface of three-layer container just after forming  
5 was rubbed 10 times by cotton cloth and the electric potential thereof was measured with a static electricity detector (SV-511, of Japan Static Co., Ltd.).

(b) The three-layer container was kept at 40°C and 80% relative humidity atmosphere for 24 hours, and then after rubbing  
10 10 times the surface of the container by cotton cloth, the electric potential on the surface was measured with the static electricity detector (SV-511, of Japan Static Co., Ltd.).

(2) Adhesion of shavings of dried bonito

(a) After the surface of three-layer container just after forming was rubbed 10 times with cotton cloth, shavings of dried bonito were brought near the surface and their adhesion state  
15 was observed.

(b) After the three-layer container was kept at 40°C and 80% relative humidity for 24 hours, the surface was rubbed 10 times with cotton cloth, shavings of dried bonito were brought  
20 near the surface and their adhesion state was observed.

A : not adhered at all

B : adhered to some extent

C : adhered in plenty

25 (3) Processability

Processability was evaluated with a ratio of load when the compositions 1 to 3 were extruded with a 30mm $\phi$  extruder

equipped with the three-layer blow-molding machine against to the permissible upper limit of load of the extruder.

a : less than 30%

b : 30% or more

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(Examples 1-5, Comparative Example 1)

Three layer containers having inner volume of 100ml and having layer construction, total thickness and thickness ratio shown in Table 1, were formed using a three-layer blow-molding machine. And evaluation results of antistatic properties and processability are shown in Table 1.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Comparative Example 1
Layer construction	Outer layer	Composition 1 HDPE	HDPE	HDPE	Composition 3 HDPE	HDPE
	Middle layer	HDPE	Composition 1 HDPE	HDPE	HDPE	HDPE
	Inner layer	HDPE	HDPE	Composition 1 HDPE	Composition 2 HDPE	HDPE
Total thickness of 3 layers mm	1.1	1.1	1.1	1.1	1.1	1.1
Thickness ratio (Outer layer:Middle layer :Inner layer)	1:1:4	1:1:1	1:2:3	1:2:3	1:1:8	1:1:1
Electric potential						
Just after forming	1	25	1	3	—	—
After kept at 40°C x 80%RH	0	5	0	3	—	—
Adhesion of shavings of dried bonito						
Just after forming	A	C B	A	B A	C A	C C
After kept at 40°C x 80%RH	a	a	a	a	a	a
Processability	a					

### Industrial Applicability

The present invention can provide a resin composition superior in anti-static properties, processability and compatibility. The resin composition can be used singly, e.g. 5 as single layer article, or as multi-layer article with another material, for example, as film, tape, sheet, tube, pipe, bag, container such as blow-molded container, rod, various injection-molded articles, various blow-molded articles, etc. Especially the resin composition is useful for a packaging 10 material. A bag or multi-layer container having an outer layer comprising the resin composition of the present invention is superior in anti-dust properties. A bag or multi-layer container having an inner layer comprising the resin composition of the present invention can be used as a packaging material having 15 an excellent heat sealability and resistance to static adhesion. Among them the bag or multi-layer container having an outer layer comprising the resin composition of the present invention can be formed into a bottle superior in visual properties having a low surface reflection gloss and silky appearance having high 20 haze as well as superior in anti-dust properties.

In addition, the multi-layer article as described above can be used for applications such as electric and electronic materials including an adhesive tape or film for semiconductor such as dicing tape substrate, a back grind film, a marking film, 25 IC carrier tape and tape for taping electronic parts; food packaging materials; hygiene materials; protection films (for example, a guard film or tape for glass, board of plastic or

metal, or lens), a steel wire coating material, a clean room curtain, wall papers, mats, flooring materials, bags in flexible containers, a containers, shoes, a battery separator, a water-permeable film, an anti-fouling film, an anti-dust film,  
5 a film substituting PVC, tubes or bottles for various cosmetics, detergent, shampoo, rinse etc.

The molded articles or aforementioned multi-layer articles of the resin composition of the present invention can be used by forming adhesive layer on its one side or both sides. As such  
10 an adhesive layer, a layer of rubber type, acrylic polymer type or silicone type adhesive can be cited. Further the molded articles or aforementioned laminates of the resin composition of the present invention can be used by laminating on various kinds of substrates such as a biaxial oriented film or sheet  
15 of polyethylene terephthalate, polyamide or polypropylene; and materials including board-shaped articles of an acrylic resin, polycarbonate, a styrene polymer such as ABS or polystyrene, polyacetal etc. for utilizing its anti-static properties and other properties. When the molded articles or aforementioned  
20 multi-layer articles are used as surface materials, they can be laminated on a substrate mentioned above directly or through an adhesive layer.